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ELECTRON MICROSCOPY OF TUNGSTEN DISULPHIDE INORGANIC NANOMATERIALS

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14. ABSTRACT

Transmission and scanning electron microscopy studies of tungsten disulphide nanomaterials revealed nanotubes and onion-like structures. An electron diffraction pattern confirmed the lattice image of this nanotube. The tungsten disulphide nanomaterials exhibiting this kind of nanotubes will be useful as solid lubricant materials.

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INTRODUCTION

An inorganic nanotube is a cylindrical molecule similar to a carbon nanotube. Inorganic nanotubes have been observed in some mineral deposits. Linus Pauling suggested the possibility of curved layers in minerals in 1932 (ref. 1). The synthetic inorganic nanotubes composed of tungsten disulfide (WS_2) were first reported in 1992 (ref. 2). The purpose of this report is to describe the micro structural characterization of WS_2 inorganic nanotubes. This crystalline powder material was synthesized by the chemical vapor deposition method of decomposition of tungsten hexacarbonyl over sulphur vapor in inert gas flow. The reaction takes place between pure tungsten nanoparticles and sulphur vapor. The shape, size distribution, structure, and phase composition depends on the experimental parameters. The transmission and scanning electron microscopy together with energy dispersive x-ray analysis revealed the structure of the nanoparticles with spherical shapes. The WS_2 nanoparticles will be very useful as a solid lubricant material because of its multi layers structure and hence could be applicable for gun barrel and other weapon systems.

SPECIMEN PREPARATION

A small amount of powdered WS_2 was mixed in hexane solution. This insoluble mixture was shaken very well and a small amount of this solution was dropped on a 200-mesh carbon coated copper grid and dried at room temperature. This specimen was then placed in a single tilt specimen holder and inserted in a Philips 420 transmission electron microscope (TEM). For scanning electron microscopy (SEM), the powdered sample was taken on a stub coated with adhesive.

RESULTS AND DISCUSSION

A scanning electron micrograph from this WS_2 powdered sample shown in figure 1 reveals 'onion like' (ref. 3) particles ranging in size from 5 to 100 μm. These particles contain plenty of needles like those that structures, which are magnified from 200X to 800X (fig. 2). A single WS_2 particle with a substantial number of inorganic nanotubes as indicated by an arrow is shown on the surface of this particle. The energy dispersive spectroscopy (EDS) analysis taken from this particle is shown in figure 3. The composition of W and S is about 78.6% and 21.4%, respectively. At 1500X magnification, the SEM taken from the same particle shows a bundle of nanotubes with different diameters and lengths (fig. 4).

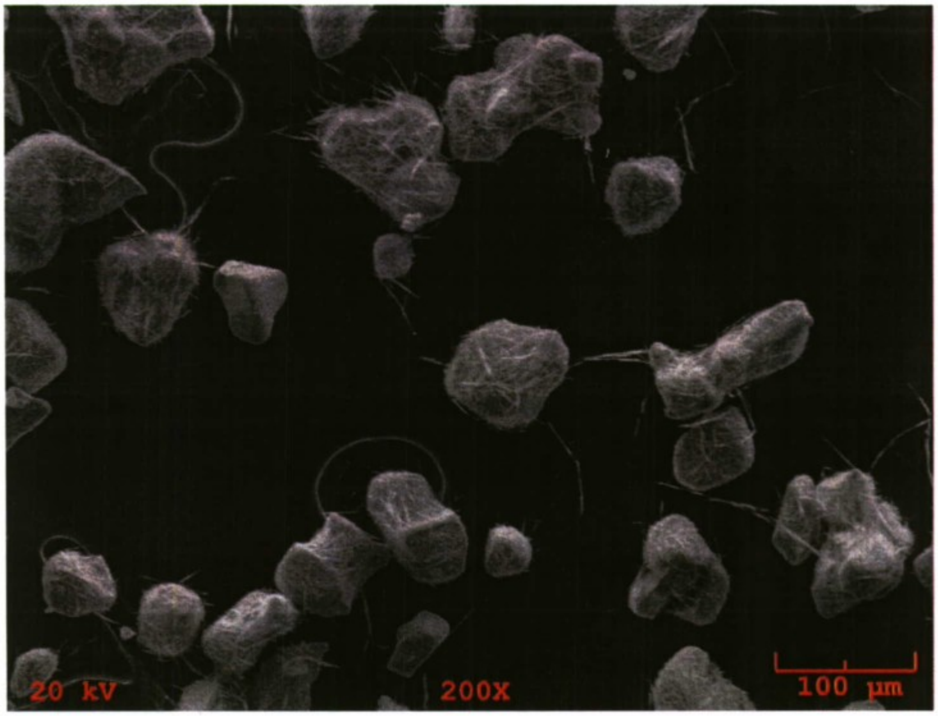


Figure 1
SEM showing WS_2 particles

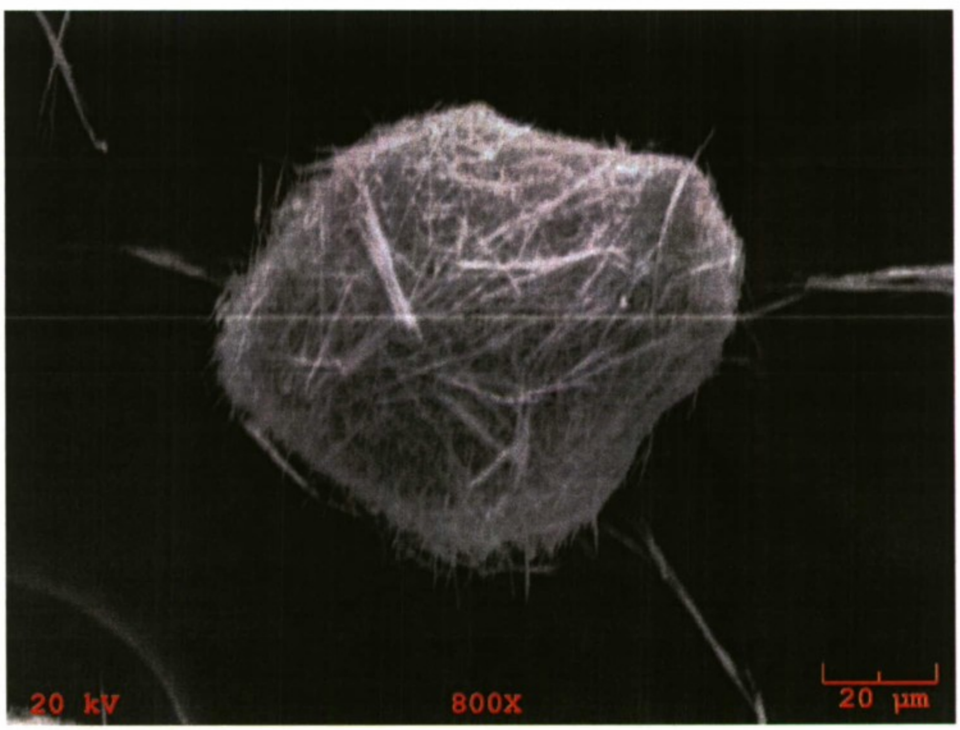
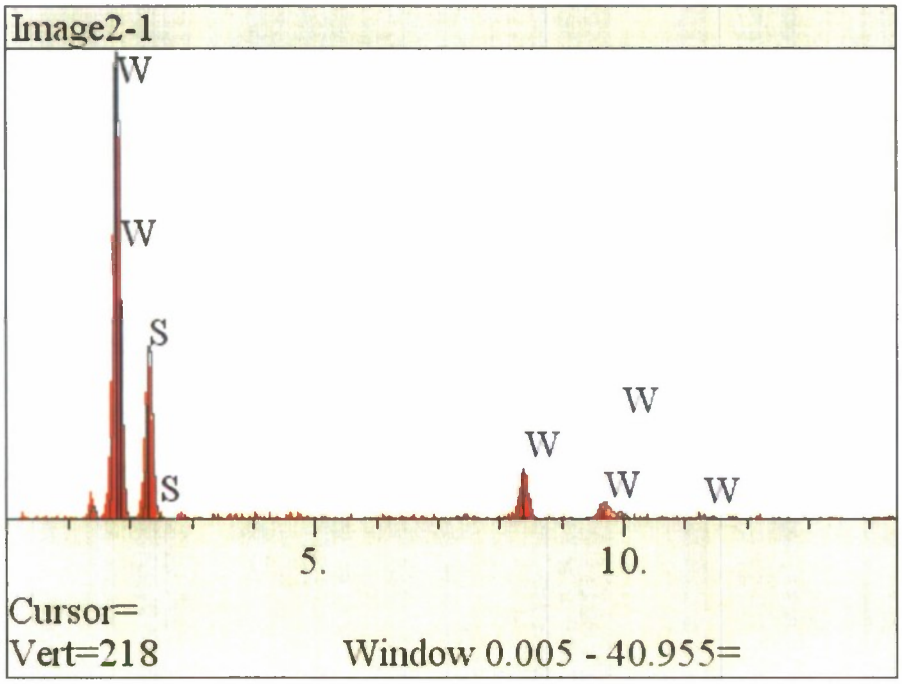


Figure 2
SEM showing WS_2 nanotubes indicated by an arrow at lower magnification

The EDS analysis taken from this particle shown in figure 2 is given in figure 3.



Elt.	Line	Intensity (c/s)	Error 2-sig	Conc	Units	
S	Ka	10.55	0.685	21.436	wt.%	
W	La	3.31	0.384	78.564	wt.%	
				100.000	wt.%	Total

KV 20.0
Takeoff Angle 35.0°
Elapsed Live time 90.0

Figure 3
EDS spectrum from WS_2 powder particles showing K and L lines from tungsten and sulfur elements

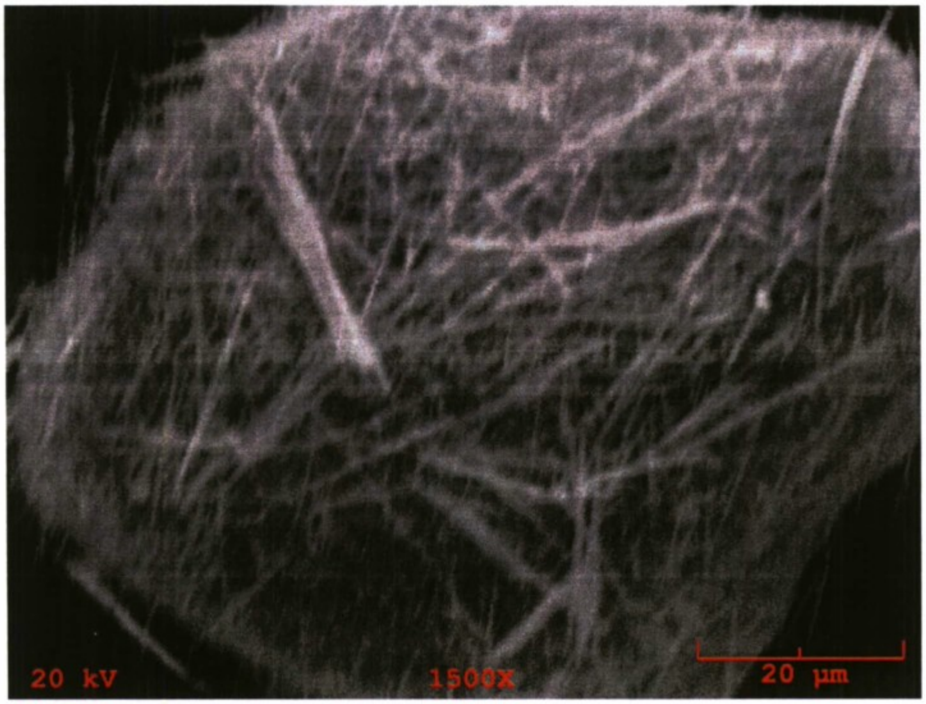


Figure 4
SEM of WS_2 particle showing its surface morphology composed of nanotubes at higher magnification, 1500X

The TEM reveals the microstructure of the WS_2 when the electron beam penetrates the particle. Thus, a TEM not only shows the image of the internal structure, but also crystalline and defect structures such as dislocation, etc. of the particle. One such TEM of a single nanotube is shown in figure 5. It is interesting to note that this single nanotube is curved, which was predicted in reference 1. This nanotube is approximately 10 μm in length and 0.1 μm diameter. An arrow is pointed to a sharp minute crystalline particle embedded in the non-crystalline hexane network represented by a large number of grey spots. The seven layers of concentric cylinder multi-walled TEM was previously published in the literature (ref. 4). The present TEM (fig. 5) is a single walled nanotube, but with a high-resolution electron microscope, this micrograph perhaps could reveal a multi-walled nanotube.

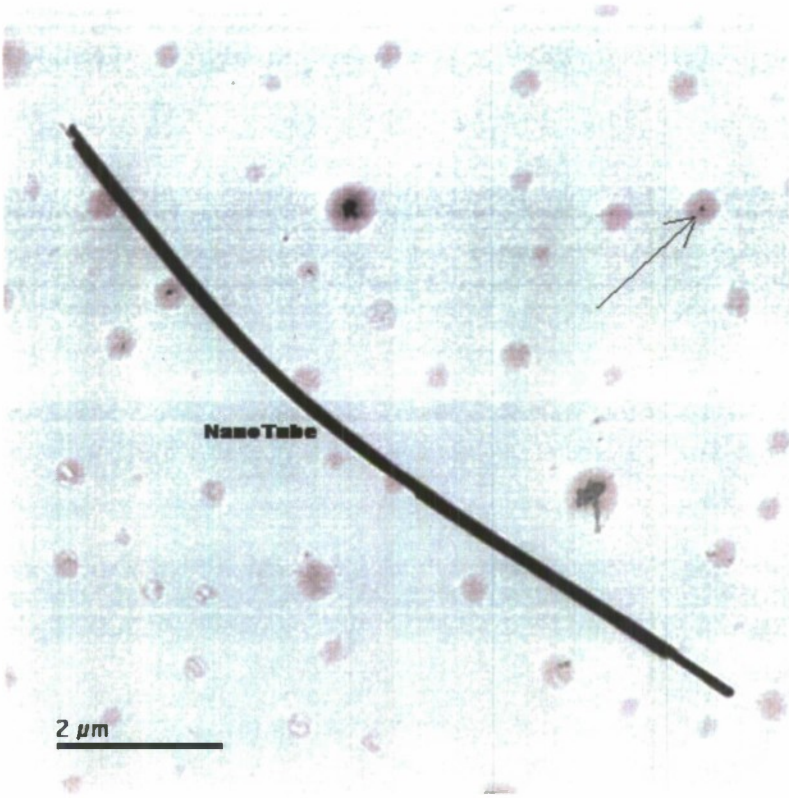


Figure 5
TEM of single nanotube obtained from WS_2 powder sample
(The arrow is pointing to a minute powder sample.)

A selected area electron diffraction pattern [SAED (fig. 6)] was taken from this single nanotube to be sure that this originated from the WS_2, not from the hexane solution or carbon coating. This spotty electron diffraction pattern confirms the crystalline structure of the WS_2 powdered nanomaterials. It should be noted that the diffraction patterns from carbon or hexane solutions will show diffuse rings. The camera length is 180 mm at 120 kv electron beam voltage. The beam stop was used to block the center beam spot as shown in the figure 6. The electron diffraction pattern indicates spotty reciprocal lattice points arranged in an array. It was established previously (ref. 2) that this lattice image represents the polyhedral and cylindrical structures of WS_2. The diffused background on the diffraction pattern was due to the carbon coating.

Figure 6
SAED taken from the single nanotube shown in figure 5

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